M 8. MOISTURE AND TENSILE STRENGTH PROPERTIES OF STARCH-SUGAR CANE NANOFIBRE FILMS

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Abstract

There is an increasing need for biodegradable, environmentally friendly plastics to replace the petroleum-based non-degradable plastics which litter and pollute the environment. Starch-based plastic film composites are becoming a popular alternative because of their low cost, biodegradability, the abundance of starch, and ease with which starch-based films can be chemically modified. This paper reports on the results of using sugar cane bagasse nanofibres to improve the physicochemical properties of starch-based polymers. The addition of bagasse nanofibre (2.5, 5, 10 or 20 wt%) to (modified) potato starch ('Soluble starch') reduced the moisture uptake by up to 17 % at 58 % relative humidity (RH). The film's tensile strength and Young's Modulus increased by up to 100 % and 200 % with 10 wt% and 20 wt% nanofibre respectively at 58% RH. The tensile strain reduced by up to 70 % at 20 wt% fibre loading. These results indicate that addition of sugar cane bagasse nanofibres significantly improved the properties of starch-based plastic films

Introduction

Non-degradable plastics are widely used in the packaging industry because they are durable, have good chemical and mechanical properties, and are inexpensive. However, their costs are constantly increasing as a consequence of depleting global supplies of fossil fuels. There is evidence that the accumulation of non-degradable plastics harms the environment, as they are either disposed into landfill sites or incinerated (Yu *et al.*, 2006). Therefore, there is demand to replace these materials with biodegradable ones derived from plant sources (Yu *et al.*, 2006).

Starch-based polymers are one such material, becoming popular because of their low cost, their abundance, and ease with which they can be chemically modified.

Unfortunately, because starch-based polymers are hydrophilic and absorb moisture from air they cannot be used directly in many applications. Also, they have a tendency to undergo 'retrogradation' (re-crystallisation on storage) and so become brittle and fragile with time.

To overcome some of these intrinsic properties, additives (e.g. plasticisers), cross-linking agents or blending with natural fillers (e.g. cellulosic microfibres or nanofibres) have been used (Alemdar and Sain, 2008; Angles and Dufresne, 2000; Averous and Halley, 2009; Chen *et al.*, 2009; Satyanarayana *et al.*, 2009; Teixeira *et al.*, 2009). Composites of starch and cellulose fibres have been reported to have improved mechanical properties because of good fibre-starch interactions (Averous and Halley, 2009). Recently (Gilfillan *et al.*, 2012) reported on the beneficial effect of reinforcing starch films with sugar cane bagasse microfibers. As a follow-on from their work, this paper reports on the use of sugar cane bagasse nanofibres to further improve the physiochemical properties of starch film.

Materials and methods

Materials

The starch (brand named 'Soluble starch') derived from acid hydrolysis of potato starch (25% amylose and 75% amylopectin, was purchased from Sigma-Aldrich, St. Louis, MO USA. This starch was selected because it has a low amylose content to easily gelatinise. Glycerol (Merck Kilsyth, Vic, Australia) was used as the plasticiser to reduce film brittleness.

Sugar cane bagasse fibre was obtained from Racecourse Mill, Mackay Sugar Limited. It was thoroughly washed, dried and de-pithed using a 10 mm screen shaker. Once dried, the bagasse was pulped and refined to produce nanofibres.

Nanofibre preparation

Nanofibres were prepared using a pulp refining method.

Pulping bagasse

Initially the bagasse was de-lignified using the soda pulping method with a liquor/fibre ratio of 12. In this process, de-pithed, cleaned and air dried sugar cane bagasse was weighed out to 1200 g and pre-treated with 210 g of NaOH dissolved in 4 L of water, which was poured onto the bagasse and left to soak for half an hour. This pre-treatment helped initiate the breaking down of lignin in the bagasse fibres. Afterwards, the pre-soaked bagasse and NaOH solution was charged into the Parr reactor along with 8 L of water. Then the Parr reactor lid was tightly bolted onto the pressure vessel and the temperature sequentially stepped up until 170°C was reached, at 106 psi gauge pressure. The bagasse was maintained at this temperature for 70 min to complete the pulping process. The final step after removing the digested bagasse from the reactor was to wash it several times with water until the water extract became clear and free of lignin.

Refining bagasse pulp to create nanofibres

The nanofibres were produced using the paper refining method. The bagasse pulp was diluted to a 1.57 wt% aqueous slurry solution and placed in a disintegrator (mechanical blender) operated at ~7,500 r/min for 10 min to break up the pulp fibre. The final step was recirculating the disintegrated pulp slurry through a machine called a 'Valley beater' that further mechanically shredded the fibres between a metal rotor and stator head that have bars with very small clearance (1 mm or less). The Valley beater was operated for approximately half an hour, after which the Canadian Standard Freeness test (Tappi standard number T 227) reached 240 mL (Anon., 2009). That was when only 240 mL water from 1 L of pulp slurry passed through the screen. The bagasse cellulose nanofibres greatly impede the drainage of water at this point and further refining was discontinued since it would likely damage the stator and rotor surfaces of the beater through excessive wear.

The last step was to separate the nanofibres from the larger pulp fibres. The refined slurry was diluted to a solids concentration of 0.10 wt% and poured into a 1m diameter (80 L) vessel having an impeller inside with a 200 mesh (stainless steel) screen on the bottom. The dilute slurry, as it was agitated by the impeller, continuously flowed by gravity through the fine screen carrying nanofibres. Simultaneously, a flow of water equivalent to that being draining out was added to the top of the vessel to maintain a constant fluid level.

The liquid that initially drained from the tank had a misty appearance because of the presence of nanofibres. However, this liquid flow became clear after nanofibre separation reached effective completion, since few if any nanofibres were then being extracted. For each run of 80 L of 0.1 wt% solids solution, 160 L were required to be drained from the tank before nanofibre extraction was complete. The buckets used to collect the nanofibres were left to settle overnight. Fibres were concentrated by sedimentation and the clear top water was decanted off. The thick remaining nanofibre slurry was further de-watered by vacuum filtration. This final step of vacuum filtration was very time consuming because the nanofibres greatly restricted the flow of water through the filter.

The nano-pulp was kept refrigerated to prevent any microbial degradation and placed into waterproof bags to prevent moisture loss. This prevents the nanofibres from becoming damaged by possible decomposition or drying out and agglomerating.

Compositional analysis of sugar cane bagasse and nanofibre pulp

The method for determining the composition of the bagasse and nanofibre was based on a modified version of the National Renewable Energy Laboratory method 'Determination of Structural Carbohydrates and Lignin in Biomass' (Sluiter *et al.*, 2008).

Film preparation method

Starch (15.0 g) and glycerol (3.6 g) were thoroughly mixed together before 450 mL distilled water was added to prepare a 4 wt% solution. Bagasse nanofibre was then added at 0.000, 0.375, 0.750, 1.500 and 3.000 g (dry basis) loading to produce 0, 2.5, 5, 10 and 20 wt% based on a starch weight basis. Each mixture was boiled while stirring vigorously for 30 min and then allowed to cool to 75 °C before being cast on a non-stick

tray and placed in a 65 °C oven to dry. To avoid crystallisation of the cast films, a drying temperature of 65 °C was selected to help produce an amorphous film (Lafargue *et al.*, 2007). It was desirable to have an amorphous film so that the degree of crystallinity can be attributed to other processing conditions or starch properties. The cast film thickness varied between 0.25 and 0.35 mm.

Uniform films were prepared by grinding the cast films using liquid nitrogen in a mortar and pestle (i.e. cryo-crushing) and hydrating to 24 wt% moisture prior to hot pressing. Hot pressing was conducted in a brass plate mould (90 mm x 60 mm x 1 mm) for 15 min at 150 °C for Soluble starch. A force of 7.5 t (m) was applied and maintained during the cooling period until 65 °C was reached to avoid foaming of the film caused by escaping steam bubbles.

Moisture conditioning

All films were placed into a relative humidity (RH) chamber that contained a saturated aqueous salt solution of NaBr that created a 58 %RH atmosphere (Greenspan, 1976). The films were left in the chamber until they reached moisture equilibration with the 58 %RH atmosphere. The moisture uptake was measured gravimetrically from four samples.

Scanning electron microscopy (SEM)

SEM was used to determine the fibre particle size distribution and morphology. The length and diameter of the fibres will be used to calculate the aspect ratio (length/diameter) if determinable.

Wide angle X-ray diffraction and crystallinity

X-ray powder diffraction (XRD) was performed by a diffractometer (XPERT-PRO) using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å) and Cu-$K_{\alpha 2}$ radiation (λ = 1.5444 Å) at 40 kV and 40 mA with a divergent slit fixed at 0.5° and a 0.5 mm receiving slit, without using any monochomator. The scanning range was between 2θ = 4° and 2θ = 30° with a step size of 2θ = 0.0167°. Wide angle X-ray diffractograms of the starch films were made by exposing the film samples cut into approximately 15 mm × 20 mm rectangular shapes to the X-ray beam. The degree of crystallinity (X_c) of the films was determined using the method described by (Dai *et al.*, 2008) using the equation:

$$X_c = A_c / \left(A_c + A_a \right)$$

where A_c refers to the sum of the crystallized peak areas above the amorphous area and A_a refers to the amorphous area on the X-ray diffractogram.

Tensile testing

Dumbbell-shaped specimens were punched out from the freshly hot-pressed 1 mm thick starch polymer films using the ASTM Standard (Anon., 1996) Type M-III die for tensile testing. All specimens tested were conditioned in a controlled atmosphere of 58%RH at 25°C until a constant moisture weight was reached at equilibrium (~10 days). An Instron 4505 tensile testing machine equipped with a 100 N load cell for enhanced

sensitivity was used to measure the tensile stress. Soft grips were employed to help prevent the delicate starch polymer specimens from being damaged by the machine grips. A cross-head speed of 5 mm/min was used during testing.

The tensile strength (stress) was determined by dividing the force measured by the load cell by the cross sectional area of the specimen. The measure of the film's change in shape (strain) was determined by the length extension as a % of the original specimen length. The elastic modulus or Young's Modulus is a measure of the amount of stress needed to change the shape. It was calculated automatically from the initial slope of the stress-strain curve by the software used for the Instron machine. The strain at yield is the point where less stress is required to increase the strain, whereas the strain at break is the maximum strain where the film breaks.

Results and discussion

Nanofibre characterisation

The nanofibres derived from the pulp refining process are very long and have a large aspect ratio (length/diameter). However the aspect ratio was difficult to determine from the SEM photo, as shown in Figure 1. The nanofibre diameter ranged from 15 to 65 nm, with the majority of the fibres between 25 to 45 nm in diameter. It was previously reported (Bhattacharya *et al.*, 2008) that the aspect ratio of bagasse nanofibres was from 50 to 120. This aspect ratio is similar to those for nanofibres derived from wood pulp, which were from 84 to 146 (Zhang *et al.*, 2012).

Fig. 1—SEM of sugar cane bagasse nanofibres derived from the pulp refining method.

Analysis of the nanofibres was carried out using a modified procedure based on the National Renewable Energy Laboratory (Sluiter *et al.*, 2008) with results shown in (Table 1) indicated the lignin content was reduced from 28.4 wt% to 10 wt% by the soda pulping process. Some hemicellulose was removed, and this resulted in the cellulose content increasing from 41.5 wt% to 65.7 wt%. Removal of lignin and hemicellulose, the non-crystalline (amorphous) components of bagasse fibre will invariably increase the fibre crystallinity, and assist in hydrogen bonding with the starch matrix.

Table 1—Compositional analysis (wt%) of sugar cane bagasse and pulp nanofibre

Component	Bagasse* microfibre	Bagasse pulp* nanofibre [+]
Cellulose	41.5	65.7
Lignin	28.4	10.0
Hemicellulose	24.1	18.5
Ash	4.0	6.7
Total	98.0	100.9

*De-pithed sugar cane bagasse was used to produce the micro-fibres and nano-fibres.
[+]Soda pulping process used at 170°C (106 psi (g)) for 70 min.

Moisture uptake

Figure 2 shows the moisture uptake and the crystallinity of the films. The films were all conditioned at 58% RH because this is the typical humidity for most ambient conditions under which the film would be used in packaging material. The film without any fibre absorbed the most moisture at 14.1 wt% whereas all the films containing fibre, regardless of the fibre content all absorbed approximately the same 12 wt% moisture. That was only a reduction in the moisture content by ~15 wt%.

It was expected that increasing fibre content from 2.5 to 20 wt% would decrease film moisture uptake due to the cellulose fibres displacing more of the starch molecules, which are comparatively more hydrophilic. As this did not occur the increase in the proportion of lignin imparted to the starch matrix, as a consequence of the increased fibre loading, may have had a detrimental effect. It has been indicated that lignin interferes with hydrogen bonding between the fibres, glycerol and starch (Le Digabel and Avérous, 2006). The reduced moisture effect from the increased film cellulose fibre content may have been offset by an increase in moisture uptake from an increased lignin content in the starch matrix. This same result occurred when microfibers were added to the films in previous experiments by the authors (Gilfillan *et al.*, 2012). The hemicellulose present in these nanofibres may also have contributed towards moisture uptake, since hemicellulose is hydrophilic.

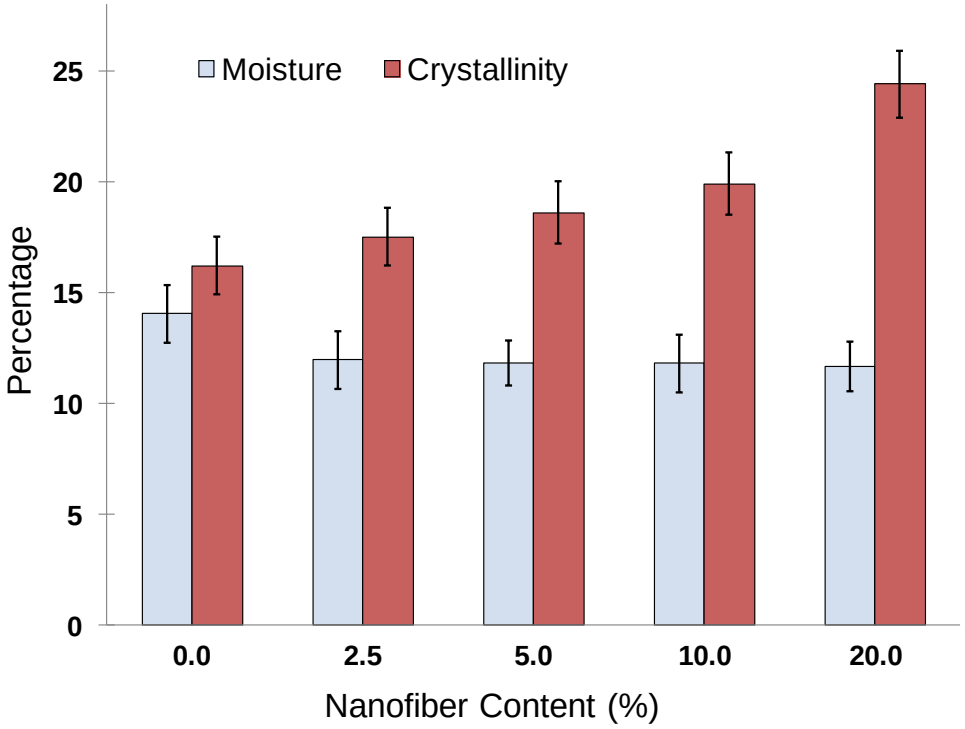

Fig. 2—Changes in moisture and crystallinity with increasing nanofibre content.

Crystallinity

Crystallinity of the film increased with increased fibre content, even though the moisture content remained relatively constant at ~12 wt% (Figure 2). (Gilfillan *et al.*, 2012) previously showed that increased film moisture uptake resulted in increased crystallinity and they suggested that this was partly explained by the increased moisture softening the film and allowing starch chains to move more freely and crystallise. However, the addition of fibre lowered moisture uptake and that will reduce starch retrogradation (crystallisation) and lower the crystallinity of the starch matrix. Furthermore if the nanofibre strongly bonded with the starch matrix this would further prevent the starch polymer chains from moving to form crystal structures.

In the case of the previous work (Gilfillan *et al.*, 2012), chain realignment took precedence over the affects of reduced equilibrium moisture during the short period of time after hot-pressing the films. However, all films were subject to the same conditions that should result in similar amounts of starch matrix crystallisation, therefore the increase of bulk film crystallinity shown in Figure 2 is mostly due to the increased crystallinity from the increased fibre content.

Tensile testing results

Tensile test results show there was a dramatic decrease in the strain at yield and strain at break with the starch-fibre films (Table 2 and Figure 3). The strain at yield and strain at break decreased by up to ~70% for film containing 20 wt% nanofibre compared

to the film with no nanofibre. This indicates that nanofibre addition significantly increased the film stiffness.

Tensile strength and Young's Modulus for the starch-fibre films are significantly higher than the films without nanofibre (Table 2). The film tensile strength increased from 3.1 to 6.2 MPa for films with 0 and 10 wt% nanofibre respectively. However, the strength decreased to 5.8 MPa with the addition of 20 wt% nanofibre. The Young's Modulus increased from 66 to 198 MPa for films with 0 and 20 wt% nanofibre respectively. Therefore, the addition of nanofibre increased the film tensile strength and Young's Modulus by up to 100% and 200% respectively.

Table 2—Mechanical properties of nanofibre reinforced Soluble Starch-based films*

Nanofibre[+] (%)	Young's Modulus (MPa)	Max. tensile strength (MPa)	Extension at max. strength (%)	Extension at break (%)
0.0	66 +/- 4.0	3.06 +/- 0.10	42.5 ± 3.5	49.0 +/- 3.8
2.5	153 +/- 9.0	4.84 +/- 0.11	32.4 +/- 2.5	39.0 +/- 2.9
5.0	173 +/- 13	5.32 +/- 0.29	27.7 +/- 1.5	31.0 +/- 2.0
10.0	181 +/- 11	6.23 +/- 0.19	19.0 +/- 2.1	20.5 +/- 2.2
20.0	198 +/- 19	5.78 +/- 0.39	13.4 +/- 2.3	14.5 +/- 2.4

*Mean of at least 7 repeats

[+]Fibre % based on the starch weight of the composite.

These results using nanofibres as reinforcing fibre demonstrate the vastly superior bonding ability they have compared with microfibres as shown in previous work (Gilfillan *et al.*, 2012). At just 2.5 wt% nanofibres, the film strength was increased to 4.8 MPa that is ~10% greater than the maximum strength of 4.4 MPa achieved by using 5 wt% microfibres. The maximum strength using nanofibres (6.2 MPa) was 42% greater than the maximum strength (4.4 MPa) achieved by using microfibres. The maximum Young's modulus using nanofibres was also 65% higher than the maximum value achieved by microfibres. The strain at yield and strain at break were both however reduced by a similar amount regardless of whether nanofibre or microfibre was used as reinforcement.

In a previous study, when sugarcane bagasse pulp fibre was used to reinforce starch-based plastic films (Vallejos *et al.*, 2011), it was found that the tensile strength increased at up to 10 wt% fibre loading but decreased at higher fibre loadings. Vallejos *et al.* (2011) suggested that bagasse fibre agglomeration and poor dispersion in the matrix took place if more than 10 wt% fibre was added. This was considered attributable to agglomeration of the bagasse pulp fibres. In this present study, it was found that the bagasse nanofibres derived from sugar cane bagasse pulp also reduced tensile strength at nanofibre loadings above 10 wt%. Therefore, it could be that agglomeration of the nanofibres begins to occur at loadings above 10 wt%. It could be considered also there

was overloading of the film when more than 10 wt% nanofibre was added and that could cause a discontinuity of the starch matrix.

The tensile strength and Young's modulus for starch/glycerol films containing up to 10 wt% wheat-straw nanofibres (based on dry wt. of nanocomposites) increased by 72 and 144% respectively (Alemdar and Sain, 2008). That was not as good a result as achieved in the present study (100% and 200% respectively). The wheat straw nanofibres had similar diameters (30 to 40 nm) and aspect ratios (90 to 110) and similar lignin contents to those of the sugar cane bagasse nanofibres.

The tensile strength for starch/glycerol films containing up to 10 wt% flax nanocrystals increased by 95% (Cao *et al.*, 2008). This increase is similar to what was obtained in the present study. However, when the amount of flax nanocrystals was increased to 20 wt% or more tensile strength continued to increase, whereas in the present study the addition of 20 wt% nanofibres decreased the tensile strength. This could be due to agglomeration of the bagasse nanofibres since they have a larger aspect ratio (and so may tend to overlap each other more easily) than the flax nanocrystals which have an aspect ratio 10 to 50. The flax nanocrystals also have sulphate groups attached to the surface that would be slightly negatively charged in solution preventing these fibres from agglomerating at higher loadings.

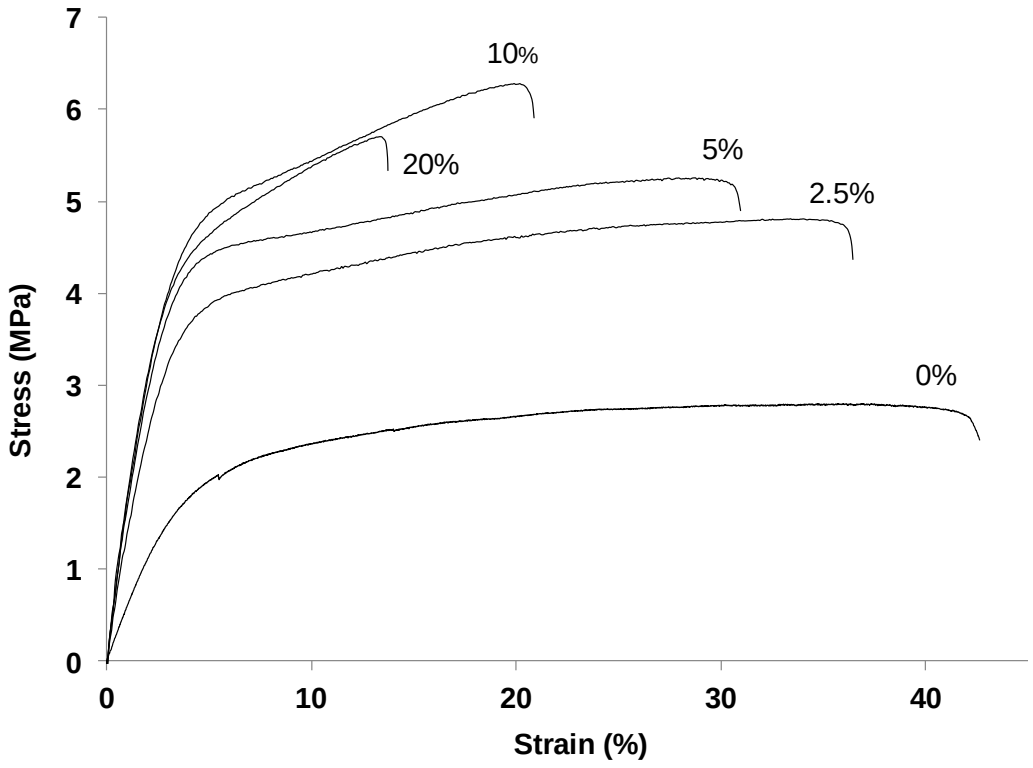

Fig. 3—Tensile stress vs strain graph for 'Soluble starch' films conditioned at 58% RH reinforced with 0, 2.5, 5, 10 and 20 wt% sugar cane bagasse nanofibre.

Conclusion

Sugar cane bagasse nanofibres, derived from unbleached pulp, doubled the tensile strength of starch-based plastic films and improved the stiffness and moisture resistance. The results were better than those for wheat-straw nanofibres and similar to those using nanocrystals derived from flax. Bleaching the sugar cane bagasse pulp nanofibres will reduce the amount of lignin and hemicellulose further and may increase the nanofibre/starch matrix bonding that could result in an even stronger more moisture resistant nanofibre-film.

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